Realizing the Sulphur-Closed Technological Processes of Metallurgical Production

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Abstract

The approach based on the use of sulphur dioxide from metallurgical off-gases as a reagent in the technologies of processing of the crude ore is considered, which allows, in specific cases, a sulphur closed cycle to be set up. The expedients are demonstrated, which enable one to reduce the body of sulphur ingress to processing with a feed stock, and to enhance the efficiency of sulphur productions now in operation.

INTRODUCTION

Traditional fields of sulphur dioxide application, as a raw material to produce sulphuric acid, sulphites, thiosulphates, bleaching and disinfecting agents, can be considerably expanded thanks to the researches, which have appeared recently. Depending on the purpose in mind, they employ sulphur dioxide as a soft oxidizer or reducer. For example, during sulphatising roasting of complex (Cu, Zn, and Pb) sulphide ores in the atmosphere of sulphur dioxide [1, 2], a sulphate product is formed, which ensures about 76 % copper and up to 99 % zinc to pass into solution upon aqueous leaching, while lead with iron remain practically completely in the insoluble residue. Pyrite dissociates under these conditions according to the scheme

$$FeS_2 \rightarrow FeS + 0.5S_2 \qquad (1)$$

$$3FeS + 2SO_2 \rightarrow Fe_3O_4 + 2.5S_2 \qquad (2)$$
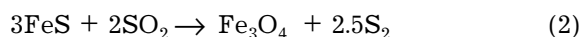
On the other hand, SO_2 is applied as a reducer to process zinc ferrite with roasted zinc concentrate [3].

The great scope of possible use of sulphur dioxide in a variety of hydrometallurgical processes is opened up: during electrolytic processing [4-6] of commercial products [7, 8], in the processes of non-ferrous metals leaching from oxidized copper ores [9] and pyrrhotinized ores [10], from oceanic (bottom) concretions [11], *etc.*

Hence, the real possibility exists of sulphur dioxide applying both in the form of the diluted or concentrated gas mixtures, and in the form of water solutions. In this case, the source of SO_2 is the metallurgical plants, which release it in the atmosphere, frequently without the proper recovery.

Issues of air-pollution control at the metallurgical plants are complicated by the lack of the system decision of all the problems that emerge during the sulphide ores processing; these problems include economic, technological,

and ecological ones. Some important aspects should be set off.

– All technological processes, including the ones of salvaging harmful exhausts of the metallurgical plants, represent to some extent the sources of harmful components emission. For example, production of elemental sulphur from "heavy" off-gases is the source of atmospheric emissions in the working area; these emissions include such compounds as hydrogen sulphide, carbon oxysulphide, carbon monoxide, the toxicity of which is considerably higher than that of sulphur dioxide; the processes of recovery of weak sulphur dioxides by means of liquid phase cause water bodies pollution.

– Implementation of chemical processes in metallurgy brings about further expansion of the infrastructure and nomenclature of material resources produced and consumed by the manufacturers (catalysts, reagents, and similar items).

– Productivity progress due to the wide use of sulphur recovery processes results in the growth of personnel number and in the need for the new auxiliary productions to be set up.

– Growth of the fixed capital, in its turn, causes amortization to increase and the profit to be essentially decreased.

It is possible to consider Norilsk Mining-and-Metallurgical Integrated Works (NMMIW) as an example.

Sulphur production at Nadyezhdinskiy and Copper Plants of the NMMIW is extremely unstable for many years. The principal reason lies in the rigid technological bonding between two inherently diverse productions, metallurgical and chemical one. Creating the "buffer" between these productions can be a solution for this situation: for example, the "buffer" in the form of liquid sulphur dioxide, which will make it possible, on the one hand, to achieve a safe recovery of the "heavy" sulphur dioxides by physical method, and on the other hand, to set up a stable production of elemental sulphur, as a recovery product most suitable for transportation.

Dressing procedures are efficient to decrease sulphur content in the concentrates of non-ferrous metals. Thus, production of the pyrrhotine concentrate as a separate product and its subsequent hydrometallurgical processing are introduced in the dressing cycle of NMMIW since 1979. This has allowed a 13 % decrease of sulphur ingress into pyrometallurgy process.

Nevertheless, all of these actions are inadequate. Application of the traditional lines of attack for the exhausts neutralization, based on building the conventional versions of recovery processes in the "tail" of metallurgical flow diagrams, is associated with huge expenses and is inefficient for the reasons listed above. Therefore, a search for new designs is appropriate to conduct in three main directions: a minimization of sulphur ingress into metallurgical process, the use of sulphur dioxide in the work cycle of the crude ore processing, and increasing the efficiency of sulphur extraction from off-gases.

MINIMIZATION OF SULPHUR INGRESS INTO METALLURGICAL PROCESS

This direction is worthy of applying the technological procedures, which enable one to minimize sulphur ingress from dressing treatment into metallurgical production, for example, by the withdrawal of low-nickel pyrrhotine product in parallel with tails of iron sulphides flotation [12]. The new reagents and regimes tested in commercial conditions allow sulphur ingress in metallurgical processing to be reduced by 20–29 %. However, with obvious simplicity, this way requires much resource and is inefficient, as the pyrrhotine product sent to long-term storage carries away therewith up to 3 % of non-ferrous metals.

The research into the process of thermomagnetic dressing of pyrrhotine has been carried out. This process is based on the fall in solubility of non-ferrous and platinum metals in the minerals of pyrrhotine group as their S/Fe atomic ratio changes to the value ≤1. Decreasing the ratio of sulphur to iron can be attained either by sulphur fixation into sulphides more stable than FeS (for example, CaS), or by creating the conditions favourable for sulphur to diffuse from pyrrhotine lattice into alternative phase, for example, into metallic iron.

Heat treatment yields nonmagnetic stoichiometrical iron sulphide, *i. e.* troilite, and the magnetic concentrate around metallic iron that
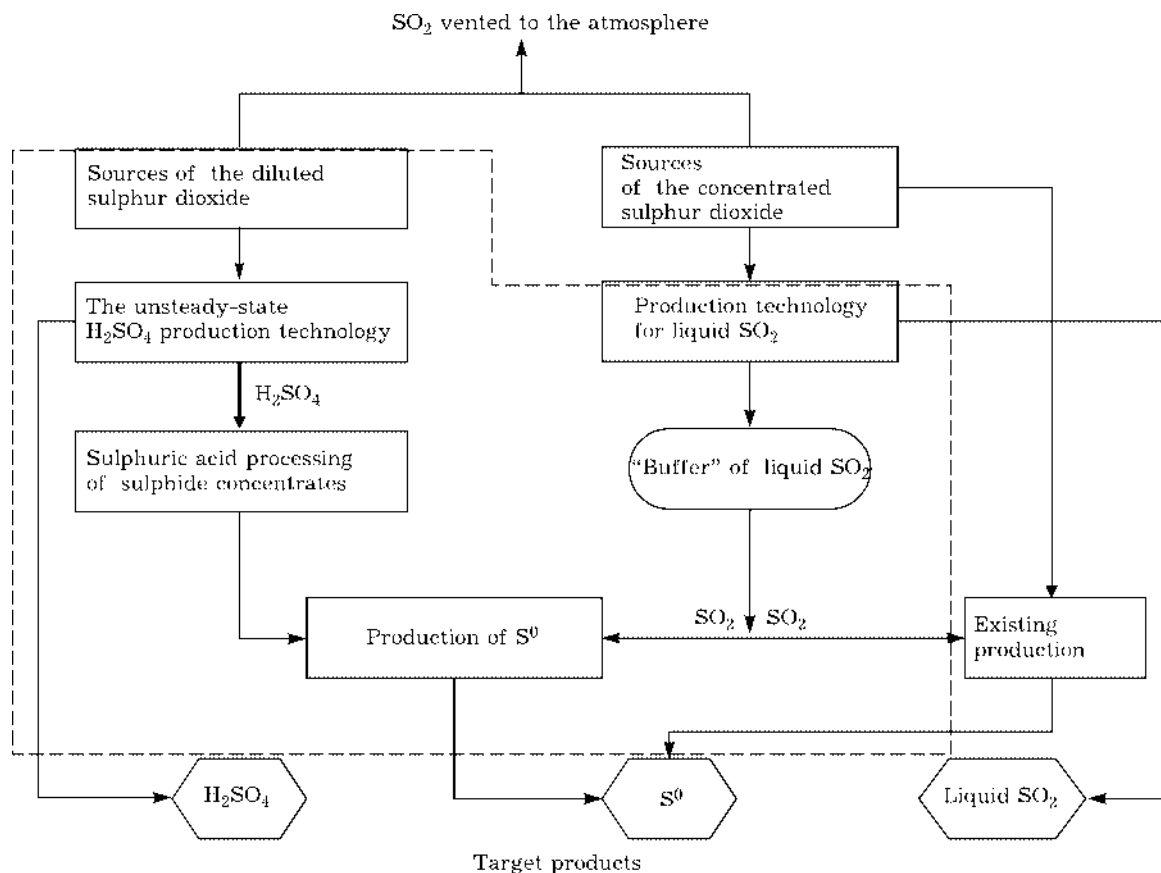
Fig. 1. Schematic diagram of sulphur cycle with the use of sulphuric acid leaching of pyrrhotine concentrate.

collects up to 95 % of nickel, cobalt, platinum metals, and up to 15−20 % of copper. Upon cooling and grinding, a cake is exposed to magnetic separation. Magnetic concentrate can be used with the flow chart of NMMIW, for example, to precipitate sulphides of non-ferrous metals from the slurry of an autoclave leaching of pyrrhotine. The non-magnetic product passes through the stage of flotation to separate the rich copper concentrate that is processed by means of conversion to yield crude copper.

Pilot-laboratory tests of this technique have verified the possibility to produce magnetic concentrate of the following content (%): Ni 5−15, Cu 0.5−1.5, Co 0.3−0.5, Fe 65−70, and S 6−8, with its yield of 15−20 % from the weight of thermally treated fusion mixture, and with extraction into this concentrate (%): Ni up to 95, Co 90, Cu 25. Copper minerals, formed during heat treatment, represent bornite solid solution.

Hence, thermomagnetic dressing of pyrrhotine makes it possible to achieve not only an extraction of up to 99 % sulphur, which comes with pyrrhotine, into the dump waste product poor in the non-ferrous metals content, but also the high extraction degree and selectivity of copper and nickel separation into the associated concentrates even at the stage of dressing treatment.

ADOPTION OF SO₂ IN THE WORK CYCLE OF CRUDE ORE PROCESSING

The second promising direction may be considered the use of sulphur dioxide from metallurgical off-gases in the work cycle of crude ore processing. This affords, on the one hand, the efficiency of the main manufacture to be raised, and on the other hand, SO_2 atmospheric emissions to be significantly reduced by means of the lower investment cost than with building of the specialized sewage treatment works.

In Nadyezhdinskiy Metal Works (NMW) of NMMIW, the use is made of the combined processing of pyrrhotine concentrate. The process

includes an oxidizing autoclave leaching, precipitation of the non-ferrous metals, which have partially passed into solution, flotation separation of sulphides and elemental sulphur from iron oxides followed by selection of the froth product to obtain the rich sulphide concentrate and commercial sulphur. Such kind of production allows one to propose two generalized flow diagrams based on the sulphur cycle set up.

The first version (Fig. 1) suggests that leaching of pyrrhotine concentrate should be conducted in sulphuric acid solutions [13]:

$$MeS + H_2SO_4 = MeSO_4 + H_2S \qquad (3)$$
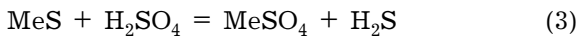
Sulphuric acid is supposed to be produced from "weak" converter gases by means of the unsteady-state process [14], while hydrogen sulphide evolving in the process is supposed to be sent to sulphur production according to currently available technology.

According to the second version (Fig. 2), autoclave oxidizing leaching is supposed to be conducted with the use of not oxygen, as in the existing production, but with pure sulphur dioxide as an oxidizer [15]:

$$MeS + 2SO_2 = MeSO_4 + 2S \qquad (4)$$
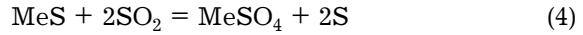
Sulphur dioxide can be obtained from "heavy" off-gases with sulphur dioxide (the volume fraction of more than 25 %) of autogenous smelting of sulphide raw material by the use of physical methods of gas mixture separation. The processes to produce the liquid sulphur dioxide by the direct compression (cooling) method [16] or involving a stage of gas hydrates formation [17] are developed. These processes allow a high recovery degree to be provided that is practically independent of the deviations of the raw stream parameters.

Based on chemical composition of pyrrhotine concentrate, specific consumption of sulphur dioxide comprises 0.5, in the first version, and 1.1 t SO_2/t of the concentrate in the second version. Application of these technologies may be restricted solely by technical difficulties in their practical realization. Taking into account the circumstance that presently sulphur recovery is practically absent in NMW, appli-
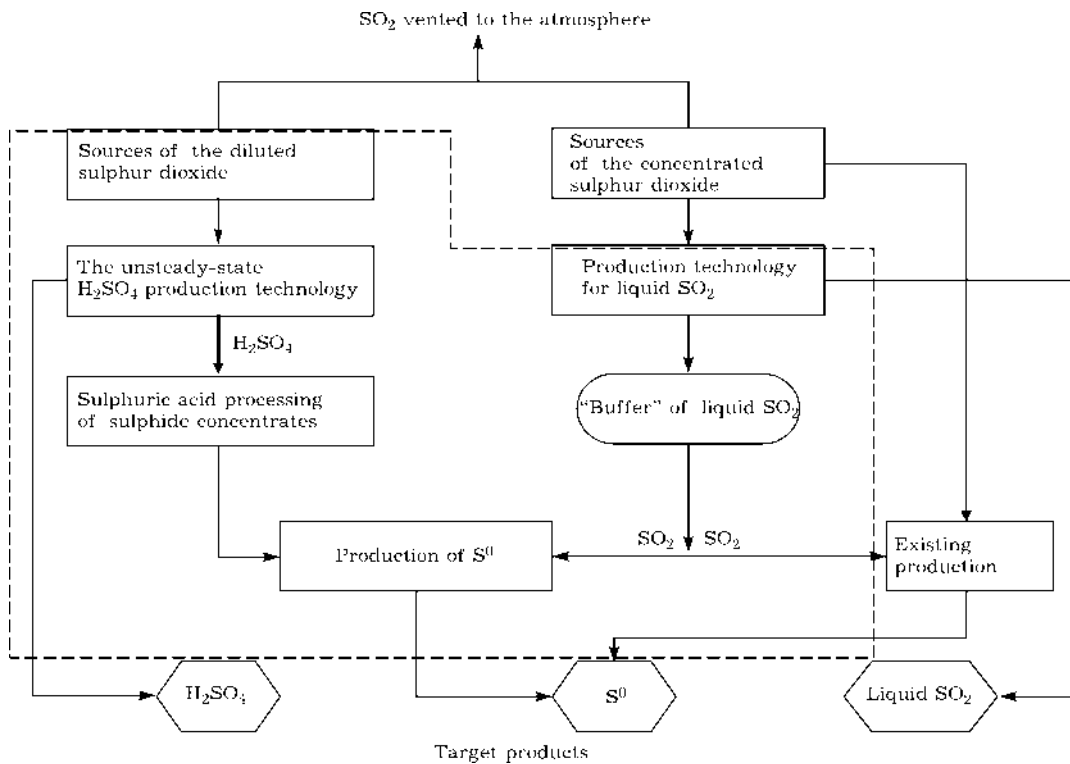

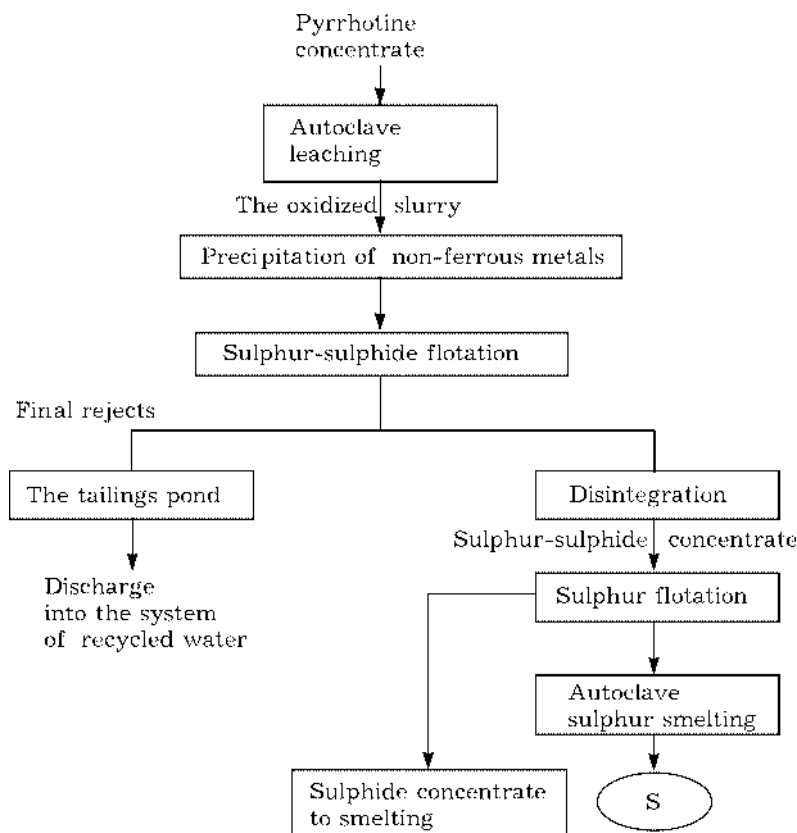Fig. 2. Schematic diagram of sulphur cycle with the use of anhydride leaching of pyrrhotine concentrate.
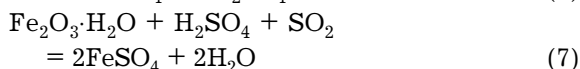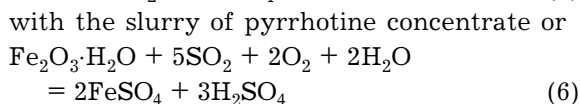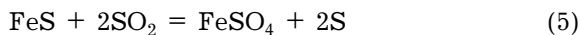
Fig. 3. Technological scheme now in operation for pyrrhotine concentrates processing.

cation of the described approach can solve a problem both for the specific plant, and for NMMIW as a whole.

The flow chart of the autoclave oxidizing leaching realized in NMMIW (Fig. 3) is associated with formation of some technical products, which hold promise to be applied as SO_2 absorbents. These products include the slurry of pyrrhotine and sulphur-sulphide concentrates, the oxidized slurry of the autoclave leaching of pyrrhotine products, the slurry from tails of sulphur-sulphide flotation and ferropurification. The estimation for an absorption capacity of these products in respect to sulphur dioxide has shown that under the similar conditions of interaction, the slurry of pyrrhotine concentrate is highly competitive with limestone suspensions. Slurries of sulphur-sulphide concentrate and of autoclave oxidizing leaching possess high absorption capacity too. Depending on type of the product, oxidation-reduction interaction of SO_2 goes by different reactions:

$$FeS + 2SO_2 = FeSO_4 + 2S \qquad (5)$$

with the slurry of pyrrhotine concentrate or

$$Fe_2O_3 \cdot H_2O + 5SO_2 + 2O_2 + 2H_2O$$
$$= 2FeSO_4 + 3H_2SO_4 \qquad (6)$$

$$Fe_2O_3 \cdot H_2O + H_2SO_4 + SO_2$$
$$= 2FeSO_4 + 2H_2O \qquad (7)$$

with the oxidized slurry of autoclave oxidizing leaching [18].

During the research of the process of sulphur dioxide absorption by iron-bearing technical products of NMMIW from the low-concentration gases (volume fraction of SO_2 was 1–5 %) on a laboratory and pilot scales, optimum absorption parameters and experimental values of kinetic parameters of the process have been determined. It has been found that the recovery degree of sulphur dioxide from weak concentration gases under the low-temperature (25–40 °C) treatment conditions stably amounts to 90 % (the maximum value is 96 %) with the average volume ratio liquid/gas equal to 0.001. The weight of absorbed sulphur dioxide recalculated to 1 t of pyrrhotine rang-

es from 80 to 216 kg. Thus, 1 t of pyrrhotine concentrate (pyrrhotine content of 75 %) is capable to provide desulphuration of at least 760 m^3 (normal conditions) of NMW gas (2.6 % SO$_2$). Consequently, when processed all low-concentration gases from NMW, it is possible to absorb no less than 40 thousand ton of sulphur per year.

An effect of preliminary treatment of slurry of pyrrhotine concentrate by weak sulphur-containing gases on the technology parameters of the subsequent stages of hydrometallurgical processing of raw material was studied by means of the pilot and semi-commercial setups with the subsequent leaching, precipitation, and sulphur-sulphide flotation. Results of semi-commercial trials have shown the enhancement of technology parameters of autoclave-hydrometallurgical processing of pyrrhotine concentrate combined with preliminary treatment by weak sulphur dioxides as compared to the existing flow diagram. The suggested version has a number of the important technological benefits.

1. Upon sulphur dioxide treatment, the slurry of pyrrhotine-containing material shows more acidic reaction (pH 2–4), which promotes a decrease in loss of platinum metals with final rejects of autoclave technology.

2. In the process of treatment of initial pyrrhotine matter with sulphur dioxide, partial leaching of ferrosulphides takes place with iron and sulphur passing into solution. This allows the productivity of the subsequent leaching stage to be raised, which provides a reserve for increasing the output of this treatment.

3. Treatment of pyrrhotine material with SO$_2$ raises the sulphur extraction degree in autoclave leaching, and promotes a deeper disintegration of oxidation-resistant minerals. This ensures, in its turn, an increase in selectivity indexes at the stage of sulphur-sulphide flotation; in particular, this increases an extraction degree of non-ferrous metals into the concentrate.

4. Consumption of limestone for ferropurification of resulting tails is less in comparison to versions, which make use of other iron oxide absorbents (sulphur-sulphide concentrate, the oxidized slurry).

5. Conditions of sulphur dioxide trapping by pyrrhotine are realized in an interval of temperatures 25–40 °C, which is responsible for simplicity of implementation and lower power expenses.

INCREASING THE EFFICIENCY OF SULPHUR EXTRACTION FROM OFF-GASES

At present, elemental sulphur is assumed an economically feasible transportable product of neutralization of sulphurous exhausts for NMMIW. Therefore, of special interest is a widespread use of catalytic processes and new types of catalysts both at a stage of sulphur dioxide reduction, and at the stages of Claus process and incineration of off-gases. This will allow a tangible reduction in energy intensity and in consumption of materials for the process.

One of the new ways is the unsteady-state Claus process. The unsteady conditions are provided by alternating the direction of reaction mixture delivery into the catalyst bed at its initial temperature (120–170 °C) [19]. Owing to thermal capacitance of periodically heated and cooled catalyst, the temperature of the reacting gases always decreases towards the outlet from the catalyst bed. The conditions close to the theoretically optimum ones are created in the reactor. The temperature of the end sites of the bed is lower than the condensation point of sulphur vapours. When a fresh reaction mixture falls on the cold catalyst (120–170 °C), the intensive reaction proceeds and is attended by sulphur condensation on the internal surface of the catalyst. This process goes on until the entire active surface is blocked, and the reaction and consequently condensation are stopped. Zone of the reversible deactivation of the catalyst will move after the thermal wave. The low-temperature zones available in the reactor that works under the non-stationary conditions theoretically enable one to reach the conversion level of up to 98 % in one catalyst bed.

From the technological point of view, the scheme of a "double" unsteady-state Claus process [20] is even more effective (Fig. 4). This scheme includes three catalytic reactors (CR-1, CR-2, CR-3), two sulphur condensers (CSC-1 and CSC-2), and four three-way gate valves for switching the gas stream (CS-1-CS-4).

Hot gas with the temperature of 350–400 °C, from the reactor of high-temperature
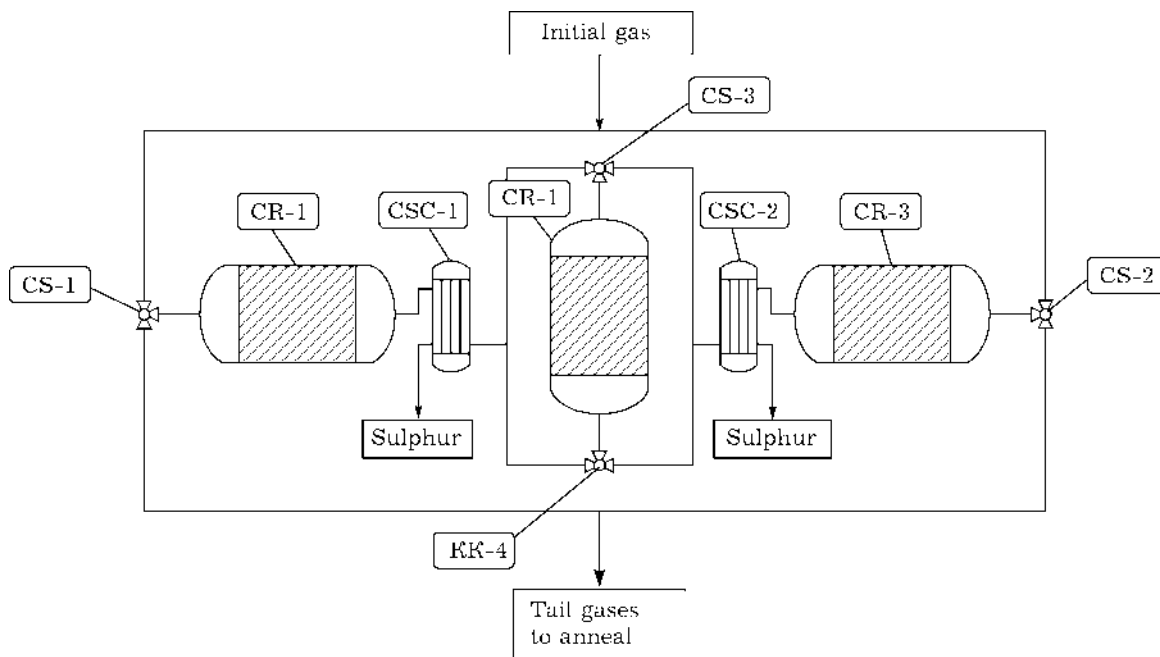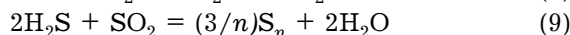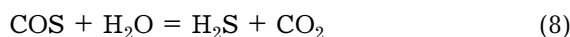
Fig. 4. Technological scheme of the "double" unsteady-state Claus process.

reduction of sulphur dioxides, enters into the reactor CR-3, where hydrolysis of COS takes place, and Claus reaction partially proceeds:

$$COS + H_2O = H_2S + CO_2 \qquad (8)$$
$$2H_2S + SO_2 = (3/n)S_n + 2H_2O \qquad (9)$$

Then gas passes through the condenser CSC-2, where it is cooled to 160−170 °C, and in so doing condensation of sulphur (formed for the most part in RG) occurs. In the subsequent process, gas enters into the reactor CR-2 that works in the non-stationary mode [19.] Unsteady conditions are also created by periodically alternating direction of gas flow through a catalyst bed by means of the system of reversing gate valves CS-3, CS-4. In these conditions, the reaction zone with a temperature of 230−250 °C is formed in the middle of the bed, and the ends of the bed play the part of heat regenerator, which allows the process to be realized without gas preheating. Sulphur, both formed in this reactor and drawn from CSC-2, partially condenses in the form of a fog on the end sides of the bed. As liquid sulphur deactivates the catalyst, an inert material may replace the catalyst in the end parts of the bed.

Gases leaving the CR-2 are cooled in CSC-1 up to 145−150 °C and are fed to the reactor CR-1 that works in the "cold bed adsorption" mode. Here, a high conversion of the mixture is achieved, and the resulting sulphur, together with the one coming from CSC-1, condenses in the catalyst bed, i. e., CR-1 works not only as a reactor, but also as sulphur trap.

Upon full deactivation of the catalyst in CR-1, "an external reverse" of the stream is made by means of the system of gate valves CS-1, CS-2. As a result, gas moves in the opposite direction. Hot initial gas from the reactor of high-temperature reduction enters first in the reactor CR-1. Sulphur in this reactor evaporates, and thereby catalyst reactivation occurs. Coincidentally with this, cooling of the catalyst in CR-2 takes place by means of gases coming from CSC-2. After a while, the mode similar to the one described above is established. Duration of a transition period is no more than 10−15 % from the time of setup operation between "external reverses".

The process proposed involves to the maximum extent the use of the equipment of the existing setup for elemental sulphur production from off-gases of Vanyukov furnaces from NMMIW Copper Plant.

CONCLUSIONS

The given analysis has demonstrated a possibility in principle for substantial decrease of sulphur dioxides emission due to recovery of both concentrated and weak sulphur dioxides of metallurgical productions within the current technology concepts. The basic advantage of the described processes is that they provide the conditions for elemental sulphur production and hydrometallurgical production, practically independent of the sources of sulphur dioxide due to creating the "buffer" of raw material that can be exemplified by both the liquid sulphur dioxide and sulphuric acid.

Additional potentialities appear with the use of techniques and technologies aimed at the preliminary removal of sulphur compounds from the initial sulphide raw material and upon the improvement of current sulphur production.

REFERENCES

1 Y. V. Swamy, A. K. Tripelhy *et al.*, *Trans. Ind. Inst. Met.*, 5 (1988) 457.

2 N. M. Temekov, I. A. Fedorov, *Izv. vuzov, Tsvet. Metallurg.*, 4 (1988) 36.

3 G. I. Sergeev, I. F. Khityakov *et al.*, *Kompleks. Ispolz. Miner. Syr'ya*, 2 (1990) 50.

4 O. A. Lyumet, L. M. Bogacheva *et al.*, *Tsvet. Metally*, 8 (1992) 17.

5 V. A. Gutin, L. V. Shmelevskaya, Kombinirovannye protsessy v proizvodstve tyazhelykh tsvetnyh metallov, Moscow, 1988, p. 167.

6 A. G. Kitay, V. I. Volkov *et al.*, *Tsvet. Metally*, 11 (1991) 15.

7 E. Petkova, *Metallurgiya*, 1 (1990) 12.

8 R. D. Apostolova, E. M. Shembel, *Elektrokhimiya*, 27 (1991) 1140.

9 S. Golar, *Turk Muhendislir cevre bilimleri. Derg.*, 14 (1990) 574.

10 A. A. Geidarov *et al.*, Problemy kompleksnogo ispolzovaniya rud (Abstracts of papers), 1996, p. 142.

11 T. Mizota, Y. Kono *et. al.*, *In Today's Technol. Mining and Met. Ind.*, (1989) 27.

12 V. V. Rybas, V. A. Ivanov *et al.*, *Tsvet. Metally*, 6 (1995) 37.

13 V. M. Zeitner, V. S. Filippov *et al.*, *Ibid.*, 10 (1972) 10.

14 G. K. Boreskov, Yu. Sh. Matros *et al.*, Tez. dokl. Vtorogo Vsesoyuz. soveshch. "Perspektivy rasshireniya proizvodstva poputnoy sery", Lvov, 1982, p. 77.

15 S. I. Sobol, G. I. Frash, *Tsvet. Metally*, 2 (1974) 14.

16 Pat. 1662921 USSR, 1991.

17 Pat. 2137707 RF, 1998.

18 A. I. Oruzheynikov, I. I. Burkova *et al.*, Proc. of Int. conf. "Khimireactor-13", part II, Novosibirsk, 1996, p. 105.

19 Pat. 911852 USSR, 1981.

20 Pat. 4131457 USSR, 1986.